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(54) **Process for the preparation of hydrocarbon fuels.**

(57) A process for the preparation of hydrocarbon fuels comprises the steps of:

- a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic hydrocarbon product;
- b) contacting the hydrocarbon product so-obtained with hydrogen in the presence of a hydroconversion catalyst under conditions such that substantially no isomerisation or hydrocracking of the hydrocarbon product occurs; and
- c) contacting at least part of the hydrocarbon product of step (b) with hydrogen in the presence of a hydroconversion catalyst under conditions such that hydrocracking and isomerisation of the hydrocarbon feed occurs to yield a substantially paraffinic hydrocarbon fuel.

EP 0 583 836 A1

Accordingly, the present invention provides a process for the preparation of hydrocarbon fuels comprising the steps of:

- a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic hydrocarbon product;
- 5 b) contacting the hydrocarbon product so-obtained with hydrogen in the presence of a hydroconversion catalyst under conditions such that substantially no isomerisation or hydrocracking of the hydrocarbon product occurs; and
- c) contacting at least part of the hydrocarbon product of step (b) with hydrogen in the presence of a hydroconversion catalyst under conditions such that hydrocracking and isomerisation of the product
- 10 occurs to yield a substantially paraffinic hydrocarbon fuel.

In the two-stage processes disclosed in the prior art, in particular GB 2077289 B and EP-B-0 147 873, the products of the hydrocarbon synthesis stage are subjected to a hydroconversion treatment. The primary objective of the hydroconversion is to convert, by hydrocracking, the high molecular weight, paraffinic products of the synthesis stage into the desired hydrocarbon fuels, for example middle distillates. However,

15 a number of additional reactions occur together with the hydrocracking reactions during the hydroconversion. In particular, the hydroconversion treatment serves to isomerise a portion of the linear paraffinic hydrocarbons, which in turn improves the properties of the hydrocarbon fuels. In addition, the action of the hydroconversion treatment is to hydrogenate the minor quantities of olefinic and oxygen-containing compounds formed during the hydrocarbon synthesis reactions and which are undesirable components in

20 hydrocarbon fuels.

In contrast to the processes of the prior art, the hydrocarbons prepared in the first stage, stage (a), of the process of the present invention are subjected to a hydroconversion in two separate and distinct stages. In the first hydroconversion stage, stage (b), the olefinic and oxygen-containing compounds are hydrogenated. However, as an essential feature of this process, the operating conditions of the first hydroconversion

25 stage are selected so as to substantially prevent hydrocracking and/or hydroisomerisation reactions from occurring.

In the second hydroconversion stage of the process of the present invention, stage (c), the desired hydrocarbon fuels are prepared by subjecting at least a part of the product of the first hydroconversion stage to a second hydroconversion treatment, in which the high molecular weight paraffinic hydrocarbons

30 are hydroisomerised and hydrocracked. Most surprisingly, it has been found that a number of major advantages result from the application of a two-stage hydroconversion regime of the present invention, compared with the single-stage hydroconversion of the prior art.

Firstly, water is formed as a product of the hydrogenation of the oxygen-containing hydrocarbons. It has been found that water produced during this reaction adversely affects certain hydroconversion catalysts,

35 leading to a reduction in catalyst performance. Secondly, it has been found that milder operating conditions are required in the second hydroconversion stage to achieve the desired degree of hydrocracking and hydroisomerisation than required in the single hydroconversion stage of the prior art process. This results in a improved lifetime of the hydroconversion catalyst and, most surprisingly, leads to a markedly improved product. In addition, the process of the present invention most surprisingly exhibits an improved selectivity

40 to valuable hydrocarbon fuels, in particular gasoil, compared with the processes of the prior art.

For the purposes of this specification, the term "substantially paraffinic" when used in connection with hydrocarbon products or hydrocarbon fuels refers to a hydrocarbon mixture comprising at least 70 %wt paraffins, preferably at least 80 %wt paraffins. Hydrocarbon fuels produced by the process of this invention typically comprise at least 90 %wt paraffins, more typically at least 95 %wt paraffins.

45 In step (a) of the process of the present invention, a feed comprising a mixture of carbon monoxide and hydrogen is contacted at elevated temperature and pressure with a catalyst active in the synthesis of paraffinic hydrocarbons. Suitable processes for the preparation of the mixture of carbon monoxide and hydrogen are well known in the art and include such processes as the partial oxidation of methane, typically in the form of natural gas, and the steam reforming of methane. The relative amounts of carbon monoxide

50 and hydrogen present in the feed may vary over a wide range and may be selected according to the precise catalyst and process operating conditions being employed. Typically, the feed contacting the catalyst comprises carbon monoxide and hydrogen in a hydrogen/carbon monoxide molar ratio of below 2.5, preferably below 1.75. More preferably, the hydrogen/carbon monoxide ratio is in the range of from 0.4 to 1.5, especially from 0.9 to 1.3. Unconverted carbon monoxide and hydrogen may be separated from the

55 synthesis product and recycled to the inlet of the synthesis reactor.

Suitable catalysts for use in the synthesis of paraffinic hydrocarbons are known in the art. Typically, the catalyst comprises, as the catalytically active component, a metal from Group VIII of the Periodic Table of Elements. Particular catalytically active metals from Group VIII include ruthenium, iron, cobalt and nickel.

Suitable catalysts for use in the first hydroconversion stage of the process of this invention are available commercially, or may be prepared by methods well known in the art, for example the methods discussed hereinbefore with reference to the preparation of the hydrocarbon synthesis catalyst.

In the first hydroconversion stage, the hydrocarbon product is contacted with hydrogen at elevated temperature and pressure. The operating temperature may typically range from 100 to 300 °C, more preferably from 150 to 275 °C, in particular from 175 to 250 °C. Typically, the operating pressure ranges from 5 to 150 bars, preferably from 10 to 50 bars. Hydrogen may be supplied to the hydroconversion stage at a gas hourly space velocity in the range of from 100 to 10000 NI/hr, more preferably from 250 to 5000 NI/hr. The hydrocarbon product being treated is typically supplied to the hydroconversion stage at a weight hourly space velocity in the range of from 0.1 to 5 kg/l/hr, more preferably from 0.25 to 2.5 kg/l/hr. The ratio of hydrogen to hydrocarbon product may range from 100 to 5000 NI/kg and is preferably from 250 to 3000 NI/kg.

The first hydroconversion stage is operated under conditions such that substantially no isomerisation or hydrocracking of the feed occurs. The precise operating conditions required to achieve the desired degree of hydrogenation without substantial hydrocracking or hydroisomerisation occurring will vary according to the composition of the hydrocarbon product being fed to the hydroconversion stage and the particular catalyst being employed. As a measure of the severity of the conditions prevailing in the first hydroconversion stage and, hence, the degree of hydrocracking and isomerisation occurring, the degree of conversion of the feed hydrocarbon may be determined. In this respect, conversion, in percent, is defined as the percent weight of the fraction of the feed boiling above 370 °C which is converted during the hydroconversion to a fraction boiling below 370 °C. The conversion of the first hydroconversion stage is below 20%, preferably below 10%, more preferably below 5%.

In the process of the present invention, the hydrocarbon product leaving the first hydroconversion stage substantially consists of high molecular weight, paraffinic hydrocarbons having a boiling point range above that of the middle distillates. At least a part of this hydrocarbon product is subjected to a second hydroconversion in stage (c) of the process of this invention, to yield the desired hydrocarbon fuel product. If desired, the entire effluent of the first hydroconversion stage may be led directly to the second hydroconversion stage. However, it is preferred to separate the low molecular weight hydrocarbons, especially the C₄-fraction, from the higher molecular weight hydrocarbons prior to the second hydroconversion stage. The separation may be conveniently achieved using distillation techniques well known in the art. At least a part of the remaining C₅ + fraction of the hydrocarbon product is then used as feed for the second hydroconversion stage.

In the second hydroconversion stage, hydrocarbon fuels are prepared from the hydrocarbon product of the first hydroconversion stage by hydrocracking and hydroisomerising the product with hydrogen in the presence of a suitable catalyst. Typically, the catalyst comprises as catalytically active component one or more metals selected from Groups VIB and VIII of the Periodic Table of Elements, in particular one or more metals selected from molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum and palladium. Preferably, the catalyst comprises one or more metals selected from nickel, platinum and palladium as the catalytically active component. Catalysts comprising platinum as the catalytically active component have been found to be particularly suitable for use in the second hydroconversion stage.

Catalysts for use in the second hydroconversion stage typically comprise a refractory metal oxide or silicate as a carrier. The carrier material may be amorphous or crystalline. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. The carrier may comprise one or more zeolites, either alone or in combination with one or more of the aforementioned carrier materials. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are silica, alumina and silica-alumina. A particularly preferred catalyst comprises platinum supported on a silica-alumina carrier.

The catalyst may comprise the catalytically active component in an amount of from 0.05 to 80 parts by weight, preferably from 0.1 to 70 parts by weight, per 100 parts by weight of carrier material. The amount of catalytically active metal present in the catalyst will vary according to the specific metal concerned. A particularly preferred catalyst for use in the second hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material.

Suitable catalysts for use in the second hydroconversion stage of the process of this invention are available commercially, or may be prepared by methods well known in the art, for example the methods discussed hereinbefore with reference to the preparation of the hydrocarbon synthesis catalyst.

In the second hydroconversion stage of this process, the hydrocarbon product of the first hydroconversion stage is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. Typically, the temperatures necessary to yield the hydrocarbon fuels will lie in the range of from 175 to 400

mulled for a period of about 10 minutes. Acetic acid (10 %wt solution) and water were added and the resulting mixture mulled for a further 10 minutes. Thereafter, polyacrylamide (Superfloc A1839, 2 %wt aqueous solution) was added and mulling continued for a further 10 minutes. Finally, polyelectrolyte (Nalco, 4 %wt aqueous solution) was added and the mixture mulled for a final period of about 5 minutes.

5 The resulting mixture was extruded using a 2.25" Bonnot extruder through a dieplate, yielding 2.5 mm trilobe extrudates. The resulting extrudates were dried at a temperature of 120 °C for about 2 hours and subsequently calcined at a temperature of 600 °C for 2 hours.

An aqueous solution was prepared comprising hexachloroplatinic acid (H_2PtCl_6 , 2.45 %wt) and nitric acid (7.66 %wt) having a pH of below 1. The extrudates were impregnated using this aqueous solution via the Pore Impregnation technique to give a final platinum loading on the carrier of 0.8 %wt. The thus impregnated extrudates were finally calcined at a temperature of 500 °C for about 2 hours.

(ii) Hydrocarbon Hydroconversion

15 The catalyst prepared in (i) hereabove was loaded into a reaction vessel. The $\text{C}_5 +$ hydrocarbon product of the hydrocarbon synthesis stage was fed to the reaction vessel at a weight hourly space velocity of 0.88 kg/l/hr, a temperature of 315 °C and a pressure of 35 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 660 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 750 NI/kg). Under the aforementioned reaction conditions, the conversion achieved, in terms of percent weight of the fraction of the feed having a boiling point above 370 °C converted to products having a boiling point of below 370 °C, was 16%, indicating that substantially no cracking or isomerisation of the feed hydrocarbon occurred.

The effluent of the reaction vessel was collected and the C_4 -fraction removed by distillation. The remaining $\text{C}_5 +$ fraction was retained and used directly in the next stage.

(C) SECOND HYDROCONVERSION STAGE

(i) Catalyst Preparation

30 A catalyst was prepared following the procedure described in Example 1(B)(i) hereabove.

(ii) Hydrocarbon Hydroconversion

35 The catalyst prepared in (i) was loaded into a reaction vessel. The $\text{C}_5 +$ hydrocarbon product of the first hydroconversion stage was fed to the reaction vessel at a weight hourly space velocity of 1.046 kg/l/hr and a pressure of 31 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 660 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 630 NI/kg). A liquid recycle rate of 0.17 kg/l/hr was applied. A conversion target of 55% (as defined in Example 1(B) (ii) hereabove) was set and was achieved by adjusting the operating temperature of the second hydroconversion stage. It was found that an operating temperature of 330 °C was required.

The effluent of the reaction vessel was collected and separated by means of distillation into a number of fractions. The properties of a gasoil fraction boiling in the temperature range of from 170 to 340 °C recovered from the effluent are given in Table 1.

45 EXAMPLE 2

By way of comparison, product from the hydrocarbon synthesis stage as described in Example 1(A) hereabove was treated to a single hydroconversion stage, operated to yield hydrocarbon fuels.

50 A sample of the catalyst prepared as described in Example 1(C)(i) hereabove was loaded into a reaction vessel. The $\text{C}_5 +$ hydrocarbon product of the hydrocarbon synthesis stage was fed to the reaction vessel at a weight hourly space velocity of 1.103 kg/l/hr and a pressure of 31 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 660 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 596 NI/kg). A liquid recycle rate of 0.23 kg/l/hr was applied. A conversion of 55% (as defined in Example 1(B) (ii) hereabove) was achieved at an operating temperature of 338 °C.

55 The effluent of the reaction vessel was collected and separated by means of distillation into a number of fractions. The properties of a gasoil fraction boiling in the temperature range of from 170 to 340 °C recovered from the effluent are given in Table 1.

(B) FIRST HYDROCONVERSION STAGE

A commercially available nickel-containing hydrogenation catalyst (60 %wt nickel; ex Harshaw Catalysts) was loaded into a reaction vessel. The C₅ + hydrocarbon product of the hydrocarbon synthesis stage was fed to the reaction vessel at a weight hourly space velocity of 1.0 kg/l/hr, a temperature of 220 °C and a pressure of 30 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 1000 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 1000 NI/kg). Under the aforementioned reaction conditions, the conversion achieved, in terms of percent weight of the fraction of the feed having a boiling point above 370 °C converted to products having a boiling point of below 370 °C, was less than 5%, indicating that substantially no cracking or isomerisation of the feed hydrocarbon occurred.

The effluent of the reaction vessel was collected and the C₄-fraction removed by distillation. The remaining C₅ + fraction was retained and used directly in the next stage.

(C) SECOND HYDROCONVERSION STAGE**(i) Catalyst Preparation**

A catalyst was prepared following the procedure described in Example 1(B)(i) hereabove.

(ii) Hydrocarbon Hydroconversion

The catalyst prepared in (i) was loaded into a reaction vessel. The C₅ + hydrocarbon product of the first hydroconversion stage was fed to the reaction vessel at a weight hourly space velocity of 1.25 kg/l/hr and a pressure of 30 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 1000 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 800 NI/kg). A conversion target of 60% (as defined in Example 4(B) hereabove) was set and achieved by adjusting the operating temperature of the second hydroconversion stage. It was found that an operating temperature of 334 °C was required.

The effluent of the reaction vessel was collected and separated by means of distillation into a number of fractions. The selectivity of the second hydroconversion stage to a gasoil fraction boiling in the temperature range of from 220 to 370 °C was 50%.

EXAMPLE 5

By way of comparison, product from the hydrocarbon synthesis stage as described in Example 4(A) hereabove was treated to a single hydroconversion stage, operated to yield hydrocarbon fuels, as follows:

Catalyst prepared as described in Example 1(B)(i) was loaded into a reaction vessel. The C₅ + hydrocarbon product of the hydrocarbon synthesis stage was fed to the reaction vessel at a weight hourly space velocity of 1.25 kg/l/hr and a pressure of 30 bars. Hydrogen was supplied to the reaction vessel at a gas hourly space velocity of 1000 NI/l/hr (that is a hydrogen to hydrocarbon ratio of 800 NI/kg). A conversion target of 60% (as defined in Example 4(B) hereabove) was set and achieved by adjusting the operating temperature of the second hydroconversion stage. It was found that an operating temperature of 338 °C was required.

The effluent of the reaction vessel was collected and separated by means of distillation into a number of fractions. The selectivity of the second hydroconversion stage to a gasoil fraction boiling in the temperature range of from 220 to 370 °C was 40%.

Claims

1. A process for the preparation of hydrocarbon fuels comprising the steps of:
 - a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic hydrocarbon product;
 - b) contacting the hydrocarbon product so-obtained with hydrogen in the presence of a hydroconversion catalyst under conditions such that substantially no isomerisation or hydrocracking of the hydrocarbon product occurs; and
 - c) contacting at least part of the hydrocarbon product of step b) with hydrogen in the presence of a hydroconversion catalyst under conditions such that hydrocracking and isomerisation of the hydrocarbon product occurs to yield a substantially paraffinic hydrocarbon fuel.

17. A process according to any preceding claim, characterised in that in step (c) the hydrocarbon product is contacted with the hydroconversion catalyst at a pressure of from 10 to 250 bars, preferably from 25 to 250 bars.
- 5 18. A process according to any preceding claim, characterised in that in step (c) hydrogen is provided at a gas hourly space velocity of from 100 to 10000 NI/hr, preferably from 500 to 5000 NI/hr.
19. A process according to any preceding claim, characterised in that in step (c) the conversion is at least 40%.
- 10 20. A process according to any preceding claim, characterised in that the light components, preferably the C₄- components, are removed from the product of one or both of the hydrocarbon synthesis of step (a) and the hydroconversion of step (b).
- 15 21. Hydrocarbon fuels whenever produced by a process according to any one of the preceding claims.

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